STRUCTURAL STUDIES OF INORGANIC OXIDIZERS

QUARTERLY REPORT NO. 2
M.R.I. Project No. 2790-C
Contract No. AF 04(611)-10215

1 October 1964 - 31 December 1964

Sponsored by
ADVANCED RESEARCH PROJECTS AGENCY
Propellant Chemistry Office
Washington, D. C. 20301
ARPA Order No. 24

Monitored by
Air Force Systems Command
Research and Technology Division
ROCKET PROPULSION LABORATORY
Edwards, California

MIDWEST RESEARCH INSTITUTE
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PREFACE

This program has been conducted under the general supervision of Mr. R. L. Hughes, Head, Physical and Inorganic Section. Dr. F. I. Metz, Principal Chemist is project leader; Dr. F. E. Welsh, Associate Chemist, has been responsible for the EPR analysis; Dr. W. B. Rose and Dr. John Nebgen are responsible for preparation and purification of materials and the visible-ultraviolet and infrared spectroscopic studies. Mr. J. Hennon has been assisting in all phases of the program. The Air Force Project Monitor is Lt. Eugene A. Irene (RPCL). This report has been prepared by project personnel.

Approved for:

MIDWEST RESEARCH INSTITUTE

F. V. Morriss, Director
Chemistry Division

28 January 1965

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I. INTRODUCTION

The compounds of interest in this study of the structure of inorganic oxidizers are: OF_2, O_2F_2, O_3F_2, O_4F_2, NF_3, N_2F_4, N_2F_2 and N_3F. Each of these compounds is a potential source of O-F or N-F ionic species. The object of the present program is the investigation of stable ions, such as NF_4^+, NF_2^+ and OF^+.

The experimental approach to structural studies has been the assumption that the ions will exist in solution. A suitable solvent system for the detection of O-F or N-F ions is the oxidizer itself. The present study has, therefore, been concerned with the analysis of ion or radical species present in the pure liquid oxidizers and in the liquid systems: OF_2-NF_3, O_2F_2-NF_3 and O_3F_2-NF_3.

II. TECHNICAL ACCOMPLISHMENTS

A. Preparation and Purification of Materials

The OF_2, NF_3 and N_2F_4 used in this investigation have been obtained commercially. The O_2F_2 and O_3F_2 are prepared (by the technique described below) from premixed commercial oxygen and fluorine.

The OF_2 is bled slowly from the storage tank through an HF trap (Fig. 1) and condensed on the cold vertical column. (The HF trap removes hydrogen fluoride and silicon tetrafluoride,[1] while the cold column separates any carbon dioxide present.) This vertical column is at 77°K and jacketed with a Dewar. The OF_2 condenses and drains below the cold region of the tube where it refluxes and slowly distills into the first liquid nitrogen trap. Following Schoenfelder's procedure for N_2F_4[2], the OF_2 is next chromatographed. Table I shows the relative elution times of the impurities found to be present. Prior to introduction into the system, the helium carrier gas is passed over reduced copper oxide wire at 500°C[3] to remove oxygen; Linde molecular sieves are used to remove water from the helium.

1/ A. G. Streng, Chem. Rev., 63 607-624 (1963).
2/ C. W. Schoenfelder, J. of Chromatography, 7, 281 (1962).
3/ K. A. C. Elliott, Can. J. of Research, 27F, 299 (1949).

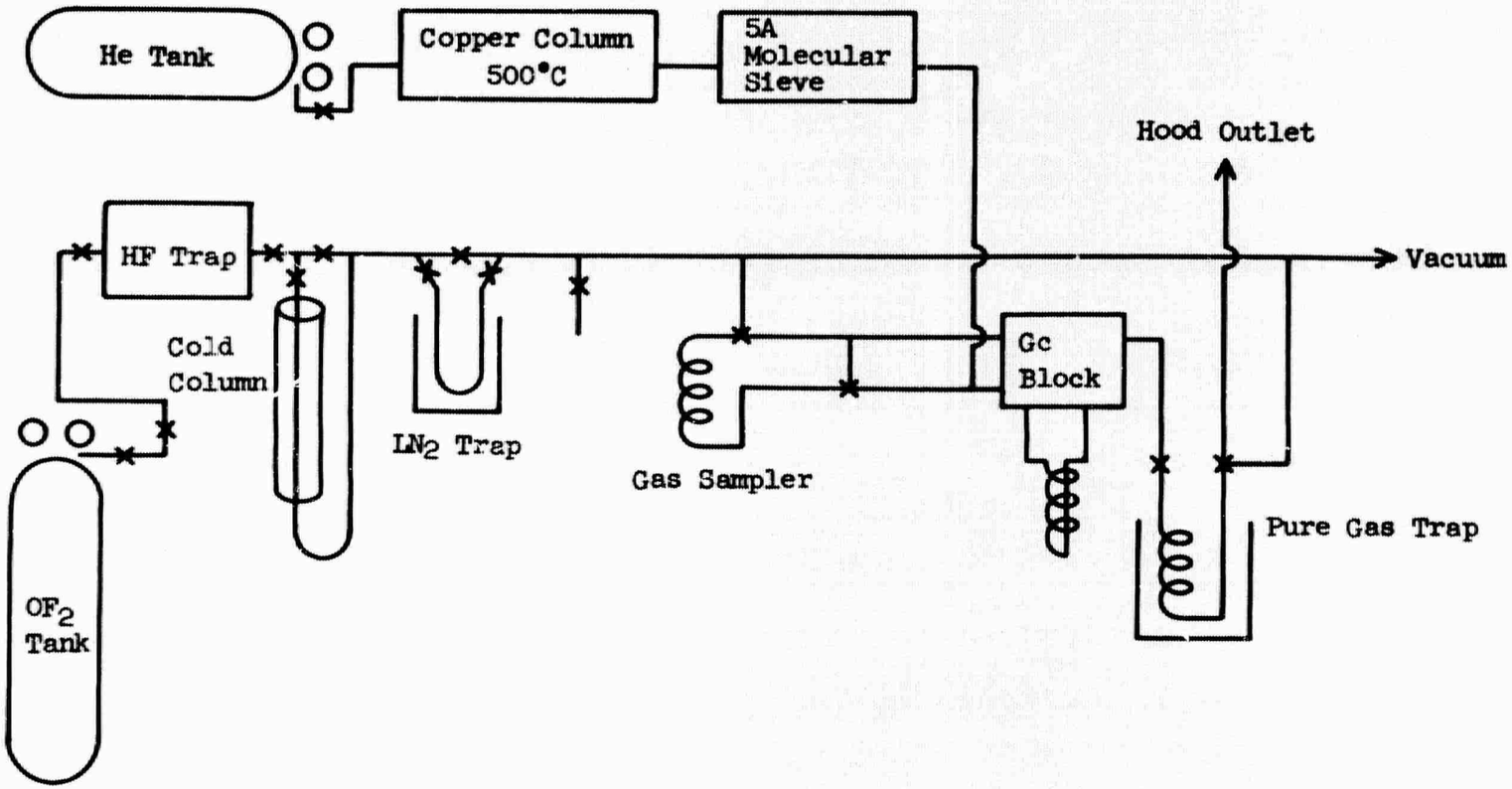

Fig. 1 - Schematic of Purification System and Vacuum Line

TABLE I

RELATIVE ELUTION TIMES ON 1/2 IN. x 10 FT. SILICA GEL COMUMN, FLOW RATE 150 ML/MIN

Substance	Elution Time of Maximim (min.)
O_2	4.7
N_2	5.1
OF_2	10.8
F_2	13.0
CF_4	16.5
CO_2	120.0
SiF_4	>120.0

$O^{17}F_2$ is being prepared for studies of the isotope effect on the OF_2 EPR signal. The electrolysis process was chosen in preference to the hydrolysis of fluorine because of the reactant requirements.[4] Of the two processes the electrolysis requires far less water, and thus reduces the cost of preparation of the $O^{17}F_2$ enriched samples.

The electrolysis technique for OF_2 production is similar to that of the "medium temperature method"[5] for the preparation of fluorine, with the exception of the presence of water Oxygen difluoride, rather than fluorine, is produced at the positive electrode if water is present in the cell. The other product at this electrode is oxygen. According to Engelbrecht[4] the water content may be as low as 1 per cent and OF_2 is 58 per cent of the gas evolved. The low water concentration requirement thus makes the process quite acceptable for this particular reaction.

The electrolyte mixture in the cell is HF(anhydrous), 72 per cent; KF(anhydrous), ~10 per cent; and H_2O, 18 per cent. The ratio of the two components (H_2O and HF) may be varied, but Engelbrecht[4] states that the optimum electrolysis is obtained with approximately 75 - 80 per cent HF.

4/ A. Engelbrecht and E. Nachbaur, Monatshefte fur Chemie, (Vienna) 90, 367 (1959).

5/ G. H. Cady, "Inorganic Chemistry," I, 1st Ed., H. S. Booth, Ed., McGraw-Hill, New York, N.Y. (1939), pp. 142-147.

The apparatus has been joined to the vacuum line as diagrammed in Fig. 2. The carrier gas (helium) and electrolysis products are passed through the HF trap,[4] a cold column (77°K)[5] and a U-trap immersed in liquid nitrogen.[6] This procedure removes HF and SiF_4 from the gas phase,[4] any substance that is solid at liquid nitrogen temperatures,[5] and those materials which are liquids at the temperature of liquid nitrogen.[6] It is in the U-tube that OF_2 is collected.

The electrolysis is performed at 0°C with a low positive helium pressure above the electrolyte. The current varies between 2 - 4 amps and the potential of the cell between 6 - 10 volts.

The reactor vessel and Dewar for the preparation of O_3F_2 and O_2F_2 are shown in Figs. 3 and 4, respectively. The reactor vessel is a modification of that reported by Tiner and English.[7] The essential modification of their design is that the Dewar joins directly to the reactor vessel. This has been shown to be an essential modification, since the transfer of the O_2F_2 and O_3F_2 (without appreciable decomposition) is extremely difficult. The O_3F_2 or O_2F_2 is removed through the bottom of the system and is collected in an appropriate storage container. The materials require no further purification.

B. Ultraviolet-Visible Absorption Spectrum of Liquid OF_2

Work is currently in progress on the ultraviolet-visible absorption spectrum of liquid OF_2. This work is being done in lieu of the flash photolysis of liquid OF_2. As was previously reported, the flash photolysis studies of liquid OF_2 were unsuccessful due to our inability to concentrate enough photolysis energy into the liquid sample.[8]

6/ J. W. Mellor, "Inorganic and Theoretical Chemistry", II, Longmans, Green and Company, New York, N.Y. (1946), pp. 516-517.

7/ N. A. Tiner, and W. D. English, "Compatibility of Structural Materials with High Performance of Liquid Oxidizers," Quarterly Report.

8/ Midwest Research Institute, Contract No. AF 04(611)-10215, Structural Studies of Inorganic Oxidizers, Quarterly Report No. 1, 1 July - 30 September 1964.

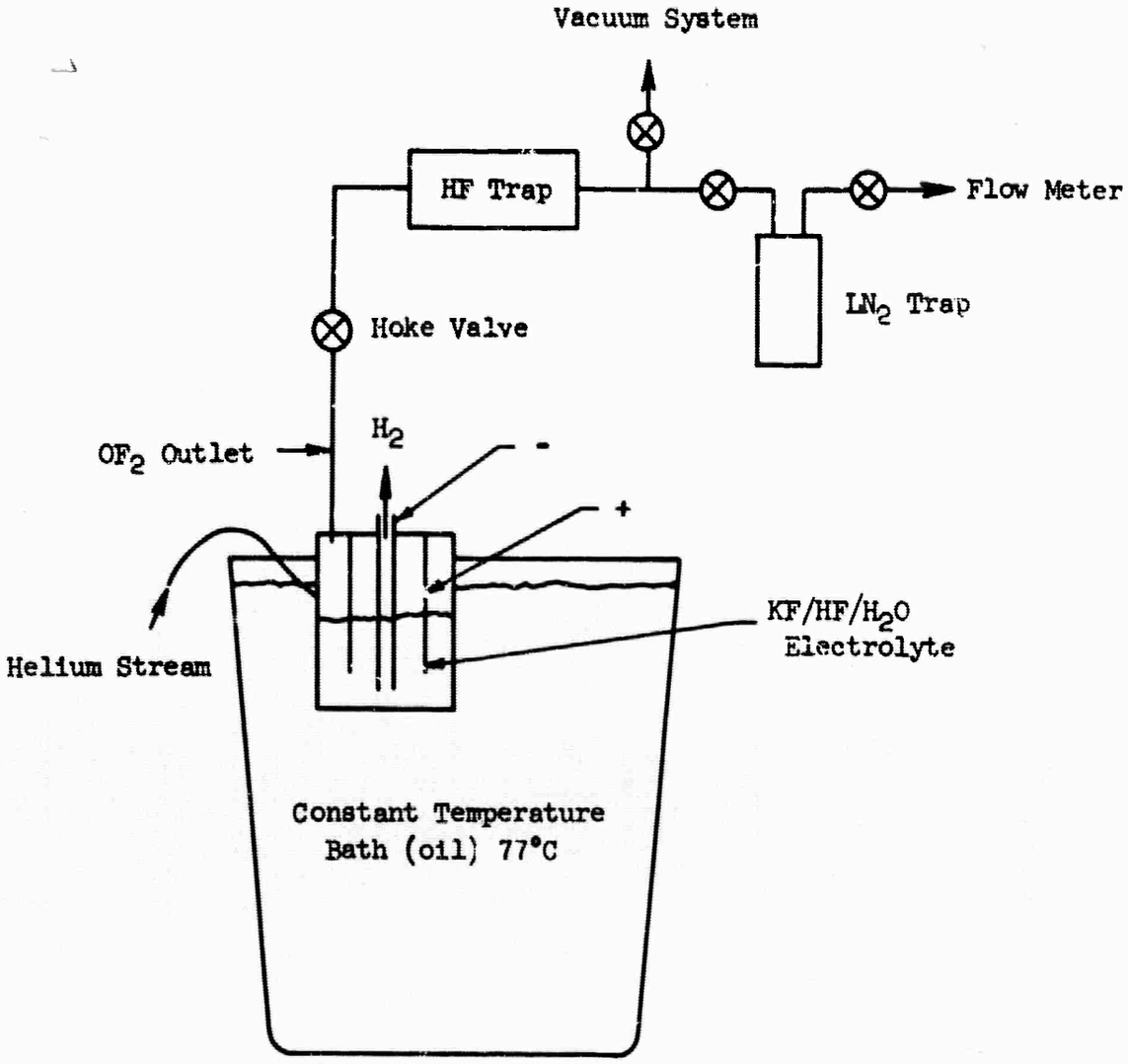

Fig. 2 - Drawing of Apparatus for Electrolytic Production of OF_2

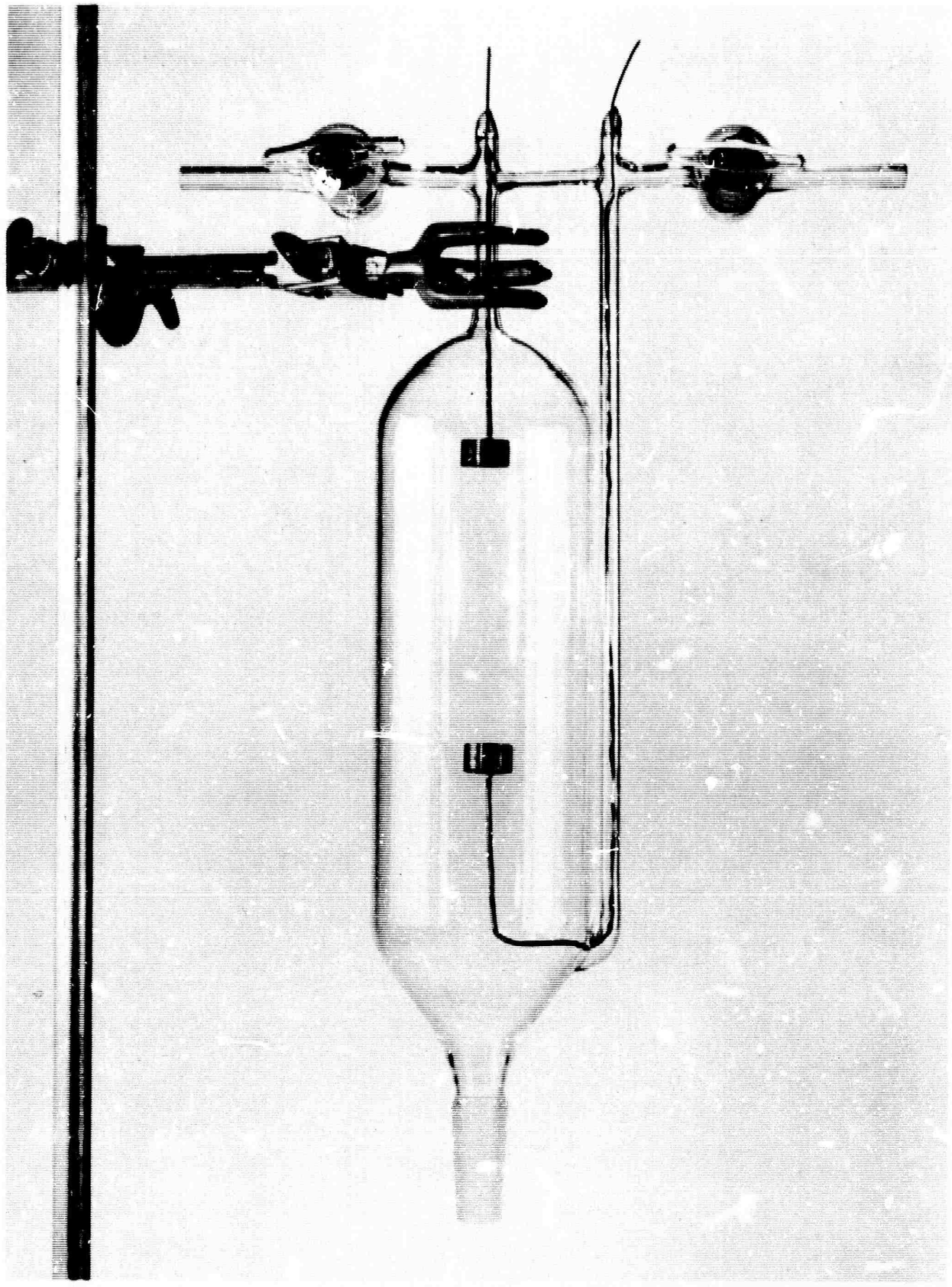

Fig. 3 - O_3F_2 (O_2F_2) Reactor Vessel

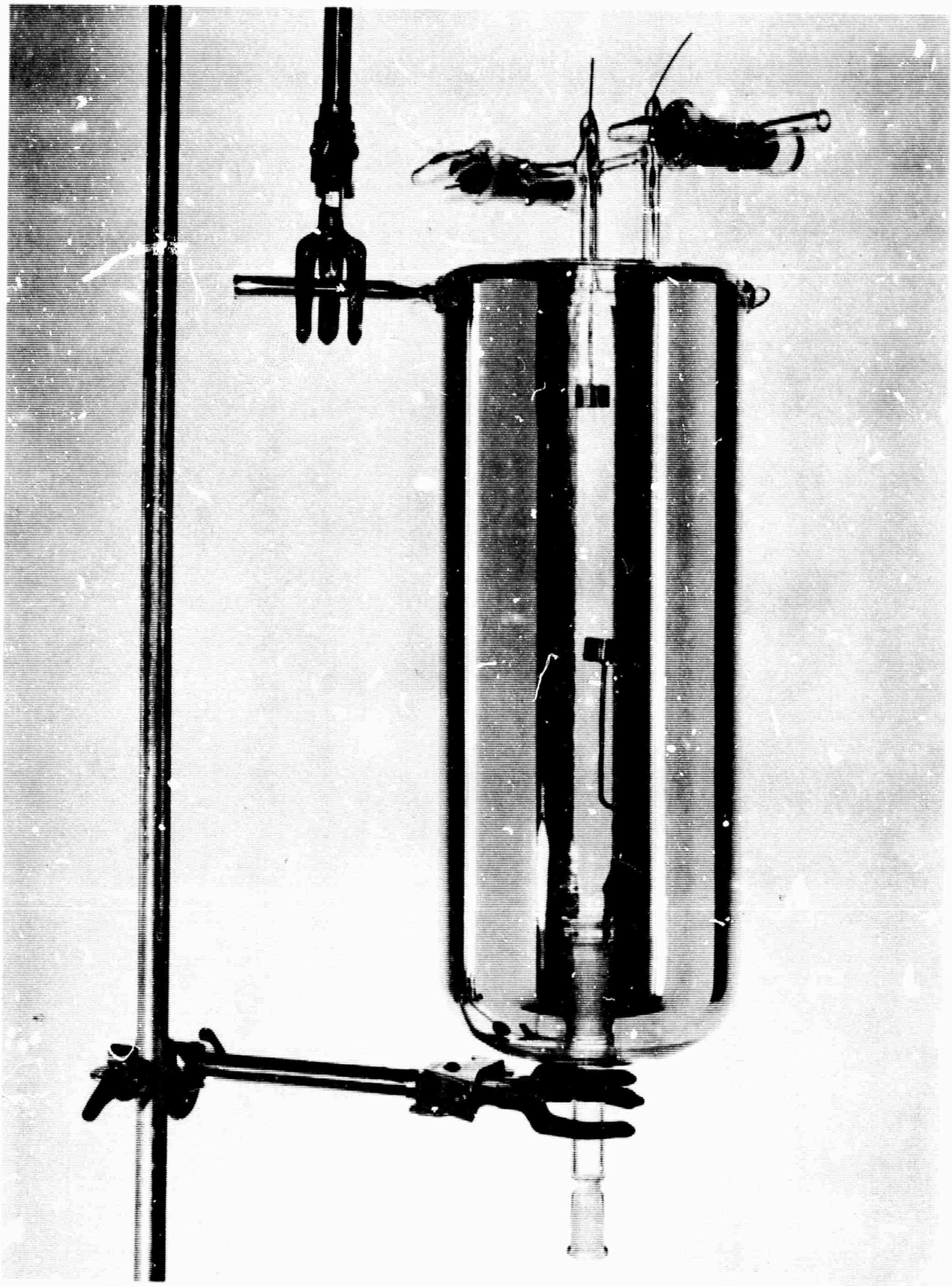

Fig. 4 - O_3F_2 Reactor Vessel and Dewar

The UV-visible spectra are taken with a Beckman DU spectrophotometer adapted to hold the low temperature cell designed for the flash photolysis studies.[8] The temperature of liquid OF_2 is 77°K (b.p. of liquid N_2). The readings are recorded point by point throughout the range of 220 mμ to 1,000 mμ. The readings are taken every 5 mμ from 220 to 400 mμ, every 10 mμ from 400 to 500 mμ, every 20 mμ from 500 to 600 mμ, every 25 mμ from 600 to 700 mμ, and every 50 mμ from 700 to 1,000 mμ. Currently we have one 2-mm. and one 5-mm. path cell available for use. Only the 2-mm. cell has been used so far. We will shortly have a 1-mm. cell available for studies in the far UV region (below 300 mμ).

The absorbances and extinction coefficients of OF_2 in the 2-mm. cell are presented in Table II. The extinction coefficients are calculated in the following manner

$$A = \epsilon \cdot C \cdot l, \tag{1}$$

where A = absorbance

ϵ = molar extinction coefficient in liters/mole-cm.

C = molar concentration in moles/liter

l = path length in cm. of sample absorbing light

The quantity A is experimentally measured, l is known, and C is calculated in the following manner:

$$C = \frac{\text{Density of } OF_2 \text{ at } 77^\circ K}{\text{Molecular weight } OF_2} = \frac{1787 \text{ g/liter}}{54.00 \text{ g/mole}} \tag{2}$$

Putting values into Eq. (2), the molar concentration becomes 33.1 moles/liter. Substituting this value for C into Eq. (1), and using a path length of 0.2 cm., the following expression is derived for calculating the molar extinction coefficient for liquid OF_2.

$$\epsilon = 0.151 \text{ A}. \tag{3}$$

TABLE II

UV-VISIBLE SPECTRA OF LIQUID OF_2 IN A 2 MM. CELL

Wavelength mμ	Absorbance A	Extinction Coefficient ε	Wavelength mμ	Absorbance A	Extinction Coefficient ε
1,000	0.029	0.00438	380	0.569	0.0859
950	0.029	0.00438	375	0.640	0.0966
900	0.029	0.00438	370	0.715	0.108
850	0.029	0.00438	365	0.814	0.123
800	0.030	0.00453	360	0.931	0.141
750	0.030	0.00453	355	1.064	0.161
700	0.031	0.00468	350	1.207	0.182
675	0.032	0.00483	345	1.351	0.204
650	0.032	0.00483	340	1.482 ?	0.224 ?
625	0.033	0.00998	335	1.594 ?	0.241 ?
600	0.034	0.00513	330	1.645 ?	0.248 ?
580	0.038	0.00574	325	1.638 ?	0.247 ?
560	0.044	0.00664	320	1.588 ?	0.240 ?
540	0.056	0.00846			
520	0.075	0.0113		Hydrogen Lamp	
500	0.104	0.0157	350	1.278	0.193
490	0.124	0.0187	345	1.459	0.220
480	0.147	0.0226	340	1.666	0.252
470	0.171	0.0258	335	1.846	0.279
460	0.199	0.0300	330	2.05	0.310
450	0.226	0.0341	320	2.18	0.329
440	0.253	0.0382	315	2.38 ?	0.359 ?
430	0.282	0.0426	310	2.44 ?	0.368 ?
420	0.316	0.0477	305	2.48 ?	0.374 ?
410	0.351	0.0530	300	2.46 ?	0.371 ?
400	0.397	0.0599			
395	0.428	0.0646			
390	0.466	0.0704			
385	0.512	0.0773			

The spectra were taken with a tungsten light source for the visible and near UV, and a hydrogen lamp for the UV regions. The energy output of the tungsten lamp is low in the UV region and a peak at 330 mμ was resolved. It is believed that this peak is not real, and is only a consequence of the great absorption (~97 per cent) of the sample at this point. Therefore, the absorbances below 340 mμ are thought to be invalid. Utilizing the hydrogen lamp resulted in a continuing increase in absorption in this region. Since the energy output of the hydrogen lamp is somewhat greater, it is believed that these readings are more valid. At 315 mμ, the absorption of light is greater than 99.6 per cent and thus can be assumed to be virtually complete. This complete absorption was noted throughout the rest of the spectrum down to 220 mμ. With the 1 mm. cell, it should be possible to go further into the UV before complete absorption is attained, and thus, a better understanding can be obtained of the region where the two lamps overlap.

The molar extinction coefficients for liquid OF_2 compare quite favorably to those reported by Glissmann and Schumacher[9] for gaseous OF_2. These authors report extinction coefficients as

$$A = \epsilon' \cdot p \cdot l, \qquad (4)$$

where A and l are the same as in Eq. (1), but p is the concentration at 1 mm. Hg pressure and 0°C, and ϵ' is a "pressure dependent" extinction coefficient. Comparable values of ϵ can be calculated from the molar concentration of OF_2 at 1 mm. Hg and 0°C. If OF_2 is assumed to be a perfect gas, the molar concentration under the described conditions becomes 5.87×10^{-5} moles/liter. The extinction coefficients reported by Glissmann and Schumacher were divided by 5.87×10^{-5} to convert them into the same molar absorption coefficients as were calculated for liquid OF_2. The corrected values are reported in Table III.

The comparison of extinction coefficients is shown in Fig. 5. Only the region in which reliable values of the extinction coefficients (600 mμ to 250 mμ) is presented. The most striking feature of this graph is that the molar extinction coefficient for gaseous OF_2 and liquid OF_2 are almost the same. There are maxima of gaseous OF_2 at 421 mμ and 294 mμ. Some unresolved fine structure is present at 358 mμ in gaseous OF_2. Fine structure is totally lacking in liquid OF_2. The slope of the curve changes in the region 390 mμ to 440 mμ indicating that possibly the maxima in the gas at 421 mμ might be affecting the extinction. We have not been able to observe spectra below 315 mμ since the absorption of light is virtually complete at this point in a 2 mm path cell.

9/ A. Glissmann, and H. J. Schumacher, Z. Physik. Chem., B24, 328 (1934).

TABLE III

UV-VISIBLE SPECTRUM OF GASEOUS OF_2

Wavelength mμ	Extinction Coefficient Reported ε'	Molar Extinction Coefficient ε	Wavelength mμ	Extinction Coefficient Reported ε'	Molar Extinction Coefficient ε
546.0	0.08×10^{-5}	0.0136	265.5	2.28×10^{-5}	0.388
513.5	0.08×10^{-5}	0.0136	257.6	3.20×10^{-5}	0.545
491.6	0.14×10^{-5}	0.0238	253.7	4.10×10^{-5}	0.698
471.5	0.18×10^{-5}	0.0306	248.2	5.70×10^{-5}	0.970
458.0	0.23×10^{-5}	0.0392	244.7	7.70×10^{-5}	1.31
445.0	0.26×10^{-5}	0.0443	239.9	10.0×10^{-5}	1.70
435.8	0.27×10^{-5}	0.0460	237.8	12.0×10^{-5}	2.04
428.0	0.32×10^{-5}	0.0545	234.5	17.5×10^{-5}	2.98
421.0	0.35×10^{-5}	0.0596	229.5	20.0×10^{-5}	3.40
404.0	0.30×10^{-5}	0.0511	225.3	27.0×10^{-5}	4.60
399.0	0.31×10^{-5}	0.0528	223.6	30.0×10^{-5}	5.11
395.0	0.36×10^{-5}	0.0613	221.0	34.0×10^{-5}	5.79
387.0	0.51×10^{-5}	0.0868	218.1	40.0×10^{-5}	6.81
380.0	0.67×10^{-5}	0.114	216.5	42.0×10^{-5}	7.15
378.0	0.84×10^{-5}	0.143	213.7	47.0×10^{-5}	8.00
365.0	0.98×10^{-5}	0.167	211.4	52.0×10^{-5}	8.85
350.0	1.10×10^{-5}	0.187	210.2	75.0×10^{-5}	12.8
334.0	1.33×10^{-5}	0.226			
313.1	1.74×10^{-5}	0.296			
302.7	1.85×10^{-5}	0.315			
296.7	1.87×10^{-5}	0.318			
292.5	1.88×10^{-5}	0.320			
289.3	1.90×10^{-5}	0.324			
280.6	1.80×10^{-5}	0.306			
275.9	1.79×10^{-5}	0.305			
270.0	2.07×10^{-5}	0.352			

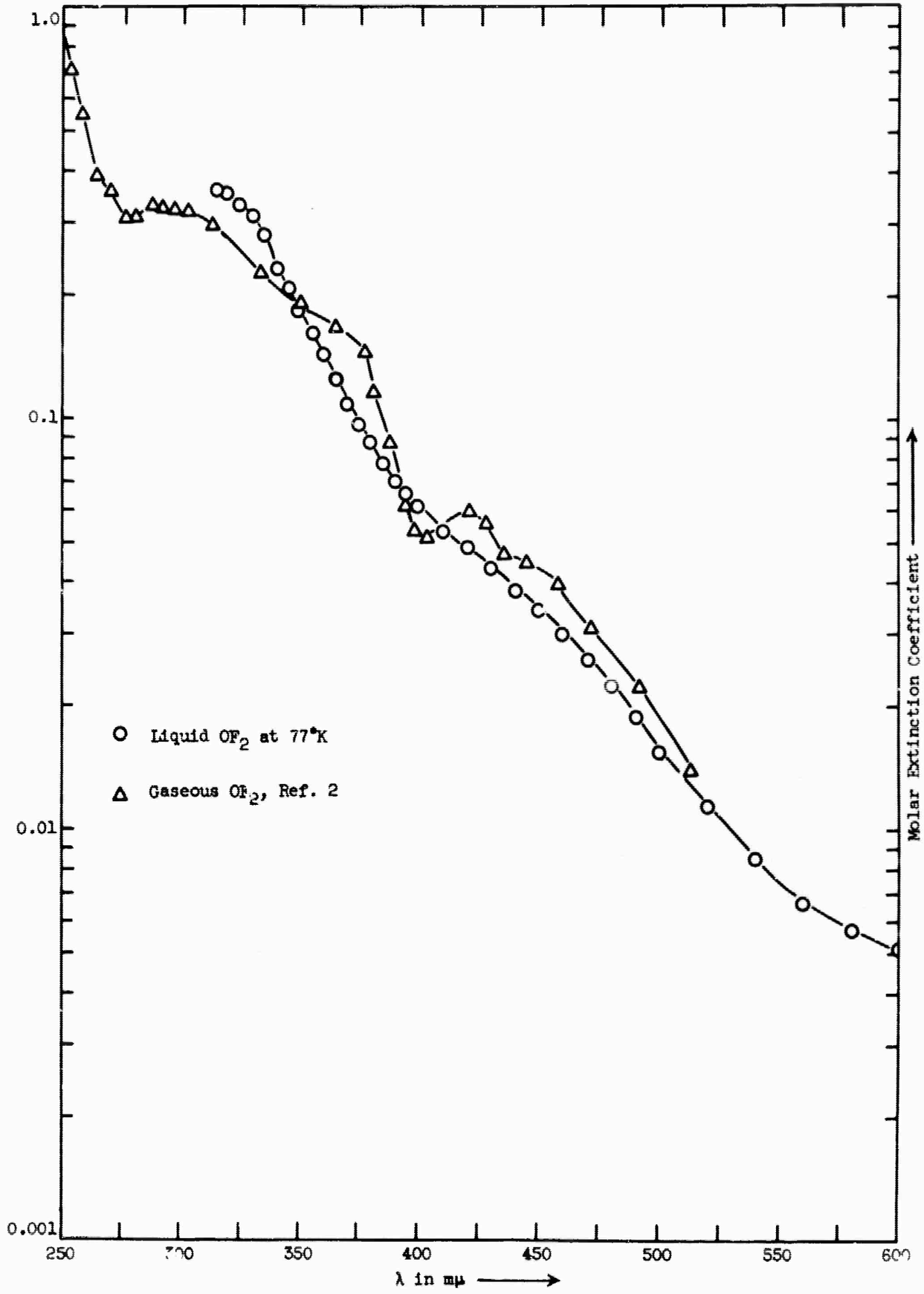

Fig. 5 - Comparison of Extinction Coefficients in Gaseous and Liquid OF_2

It may be possible to resolve some fine structure around 420 mμ if points are chosen closer together, say every 1 mμ. Similarily, changes in slope might be observed in the region between 350 and 360 mμ. With the 1 mm. cell, it may be possible to resolve fine structure below 300 mμ. On the other hand, the UV-visible spectra of liquids tend to wipe out the fine structure that appear in the spectra of gases resulting in an "envelope" of absorption. Therefore, it is equally probable that fine structure cannot be resolved in liquid OF_2.

The position where OF_2 begins to absorb light is of importance in the understanding of the photolysis reactions observed in the EPR studies. The absorption of light corresponds to electronic transitions from the ground state to an excited electronic state. This excited electronic state may be connected in some way to the appearance of radical species in photolyzed liquid OF_2. The nature of this electronic transition is not understood fully at this time.

The magnitude of the extinction coefficients is small compared to those usually associated with permitted electronic transitions. Normally, one thinks of absorption coefficients of the order of 10^3 liter $mole^{-1}$ cm^{-1}. Those which we observe in the liquid and have been observed in the gas[9] are of the order of 10^{-1} liter $mole^{-1}$ cm^{-1}. Low extinction coefficients are usually associated with forbidden electronic transitions. A forbidden transition is one where simple theory forbids the transition to occur. Since the probability is low that these transitions will occur, the absorption is weak and exhibits a small extinction coefficient. A forbidden transition may explain the weak maxima at 294 mμ, 358 mμ, and 421 mμ in gaseous OF_2.

A second conclusion can be drawn establishing that the color of liquid OF_2 is the same as that of gaseous OF_2. The extinction coefficients of liquid and gaseous OF_2 agree very closely. Therefore, we can say that the the color is the same. The apparent difference in color (gaseous OF_2 being "colorless," and liquid OF_2 being "pale yellow") can be attributed solely to the difference in concentration of absorbing species. Both liquid and gaseous OF_2 absorb in the blue-green region of the visible spectrum which would cause the transmitted light to appear a pale yellow. Since the concentration of absorbing species in gaseous OF_2 is several orders of magnitude less than liquid OF_2, the absorption of blue and green light is not noticed by the eye.

Finally, this work is in good agreement with the observations made during flash photolysis experiments.[8] There we observed virtually complete absorption below 360 mμ. Above 450 mμ, the spectrographic light output diminished rapidly so that no conclusion about the visible spectra of OF_2 could be drawn.

The effect of photolysis on the spectra of liquid OF_2 is not known. The samples which we have used have been either chromatographed or have been merely put through the HF trap and distilled without further purification. Apparently there is no difference in the UV-visible spectrum of samples prepared in these two ways. We did find, in one sample in which air had been dissolved accidently in liquid OF_2, an increase in absorbance especially in the near infrared (700 to 1,000 mμ). This increase was believed due to the O_2 species, since O_2 transitions are known in the near infrared, and since the absorbances approached those usually observed on liquid OF_2 samples with increasing time. The latter is explained by the continuous refluxing of the sample in the cell. The more volatile oxygen would reflux out and remain out of solution above the OF_2 sample. Further it was noted that if the OF_2 in the cell "bumped," the absorbance would increase again probably due to the redisolution of the O_2. If no air was brought in with the sample, or if the sample were thoroughly degassed before recording the spectra, no significant difference between chromatographed OF_2 and distilled OF_2 could be found.

During the next quarter, we shall be concerned with studying the UV-visible spectra of liquid OF_2 in the 5 mm. and 1 mm. path cells. This study will enable us to determine more accurately the extinction coefficients. Furthermore, we will look at regions of promise using smaller intervals of wavelength. This work will resolve any fine structure present in the liquid OF_2. We will also photolyze liquid OF_2 and determine whether any change occurs in the UV-visible spectrum.

Similar studies with NF_3 and NF_3-OF_2 solutions will also be undertaken.

C. Infrared Studies

The cryogenic optical Dewar and associated equipment have been previously described.[10/] The difficulties experienced with the optical windows in the variable transmission cell have prompted us to design a simple fixed thickness cell. This cell has been fabricated from two silver support strips which enclose the AgCl windows and a spacer of a desired (1,2,5, etc. mm.) thickness. The problem of cryogenic sealing has been solved by heating the

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10/ Contract No. AF 04(611)-9372, "Structural Studies of Inorganic Oxidizers," Annual Summary Report, Midwest Research Institute, RPL-TDR-64-98, 29 June 1964, pp. 1-8.

edge of the windows during the application of a thin strip of silver solder. In addition, the same basic design has been used in conjunction with the new, inexpensive, disposable (AgCl) cells which have recently appeared on the market. This latter design has not been too successful, since the cells are normally filled with a syringe, a technique we cannot use with the oxidizer materials.

The difficulties experienced in the transfer of OF_2 and NF_3 into the sample cells are currently being resolved and detailed results on this phase of the program will be forthcoming in the next quarter.

D. Electron Paramagnetic Resonance

EPR measurements have been made using a Varian V-4502 X-band spectrometer equipped with a 6-in. magnet and using 100 kc. field modulation. Frequencies used are of the order of 9.1 Gc. The sample tube is a standard 3.0 mm. I.D. quartz EPR tube connected to a stopcock and a male ground glass joint by means of a graded seal. Sample volumes are of the order of 0.05 ml. For measurements at 77°K, the sample tube is placed in a small quartz Dewar which is inserted into the cavity. Measurements in the range from 88°K to 138°K were made using a V-4557 variable temperature accessory. Peroxylamine disulfonate in a capillary affixed to the outside of the Dewar is used for the scan calibration and as a standard for the g-value determination. The total width of the peroxylamine disulfonate spectrum is taken to be 26.0 gauss and the g-value used is 2.0055.[11] The frequency is determined with a Hewlett-Packard Model X X-532-B wavemeter. The g-value of polycrystalline DPPH is determined as a check on the procedure. Concentration measurements are made relative to a Varian 0.1 per cent pitch sample in KCl, with the number of spins taken to be $3 \times 10^{+15}$ spins/cm length of sample. The accuracy of this value is estimated to be ±25 per cent.[12] However, we are more interested in relative values of the intensities of the OF_2 spectra at various temperatures (compared to the same pitch standard) than we are in absolute values of the spin concentrations.

Photolysis studies were performed using a PEK-110-100 watt high pressure mercury arc lamp. The 3660 angstrom line was selected by means of a Bausch and Lomb second order interference filter.

11/ Varian Associates, EPR at Work No. 28.

12/ Instruction Manual for V-4502 EPR Spectrometer Systems, pp. 5-11; Varian Associates, Palo Alto, California.

A sample of chromatographed liquid OF_2 prepared in the absence of light shows a strong doublet (Fig. 6) with a splitting of 13.5 gauss when photolyzed. The linewidth is temperature dependent with values in the range of 1.6 - 3.6 gauss. The line center of the doublet has a g-value of 2.0036. The line shape closely approximates a Lorentzian curve. The spectra were examined at various modulation amplitudes and microwave power levels in order to ensure that no distortion due to over-modulation or power saturation had occurred. The intensity of the doublet increases with time during photolysis. The concentration of paramagnetic species is calculated to be on the order of 10^{16} unpaired electrons per sample, corresponding to a concentration of about 0.001 mole per cent. An EPR spectrum of chromatographed liquid OF_2 prepared in normal room light is similar to that obtained from the photolyzed samples.

The change in the signal intensity with photolysis is shown in Fig. 7 for several temperatures. The rate of formation of the radical species increases with temperature. The single intensity behavior after photolysis in strongly temperature dependent. At 77°K the signal strength increases rapidly, then more slowly after the lamp is turned off At intermediate temperatures (87°K, 100°K, and 105°K) the intensity levels ff after photolysis. The curves fall off more rapidly at 121°K in the absence of light. The decay at 77°K does not proceed to zero intensity, but usually reaches a value which persists even after several days storage of the sample in the dark. The signal may be caused to vanish, or at least reach a very low level, by vaporization and recondensation of the sample in the absence of light.

Figure 8 shows the signal strength as a function of continued photolysis at 77°K. A peak concentration is reached at about 10 min. photolysis, after which time additional photolysis produces a diminution of the signal. At 24-1/2 min., the signal strength indicates the presence of approximately 10^{12} unpaired electrons. After the lamp is extinguished, the concentration immediately increases to the order of 5×10^{13} unpaired electrons. The concentration continues to increase in the absence of light. If the sample is irradiated again, the signal level rapidly drops off to its previous low value.

In general, the intensity of the EPR resonance increases with continued photolysis, reaches a maximum, and drops off to very low levels. The intensity at the maximum is temperature dependent. In a series of experiments, spectra of OF_2 were taken during 7-1/2 min. of photolysis and afterwards in the absence of light for sufficient time to observe trends in the signal intensity. The rate of formation increases with temperature. After the photolysis lamp is turned off, the intensity may increase, level off gradually, or decrease more rapidly, depending on the temperature.

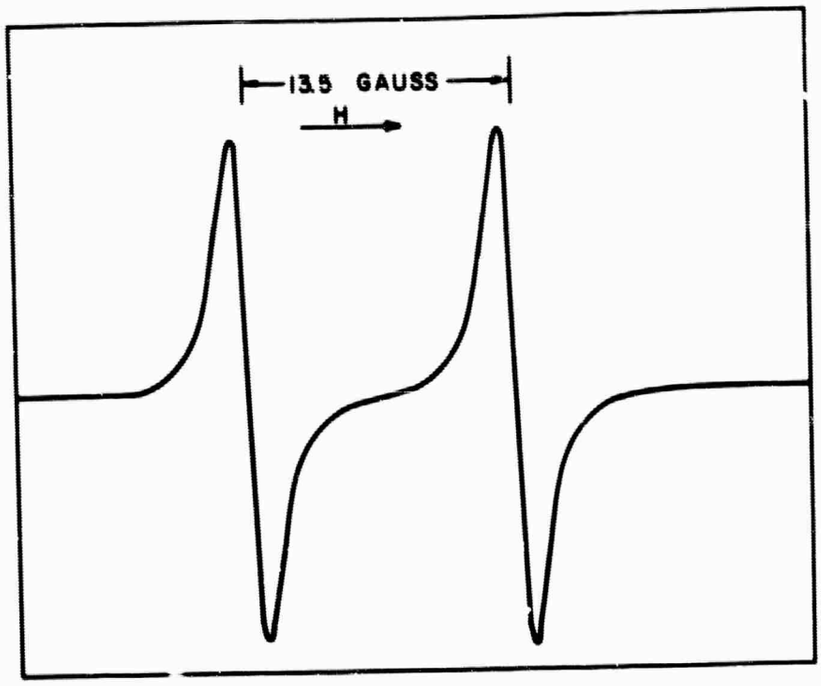

Fig. 6 - EPR Spectrum of Liquid OF_2 at 77°K

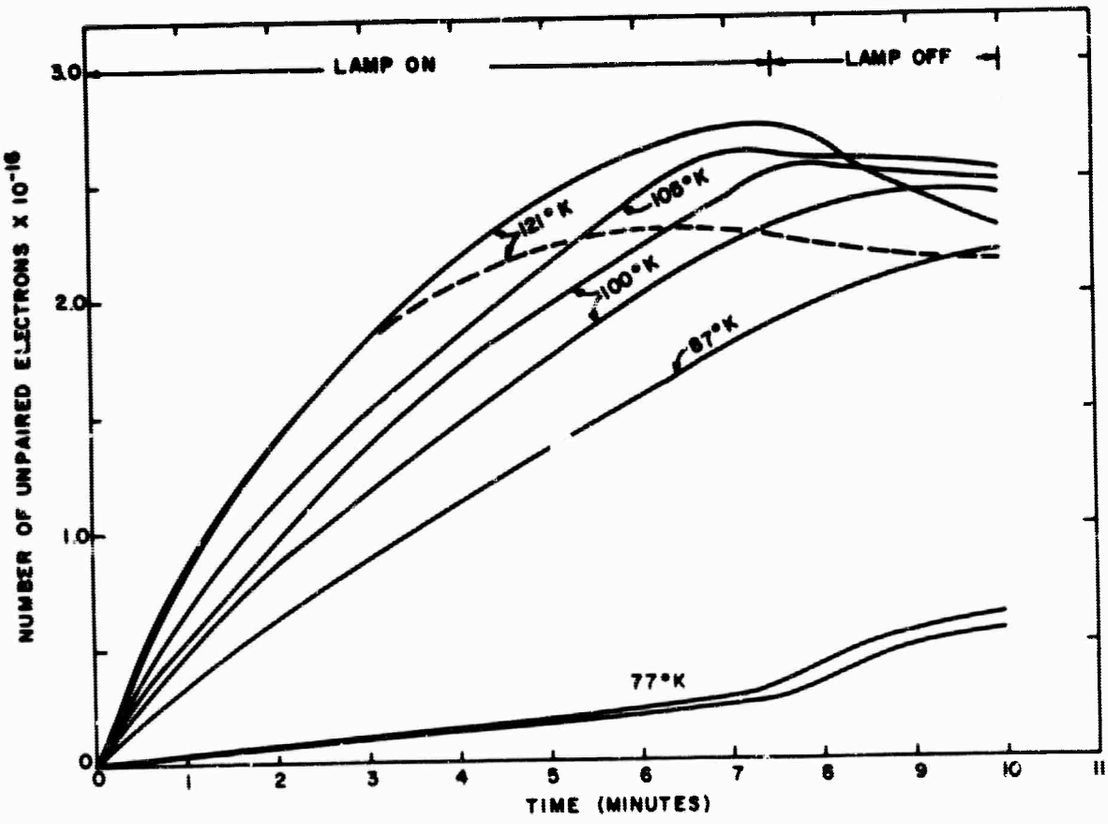

Fig. 7 - Photolysis of Liquid OF_2 as a Function of Temperature

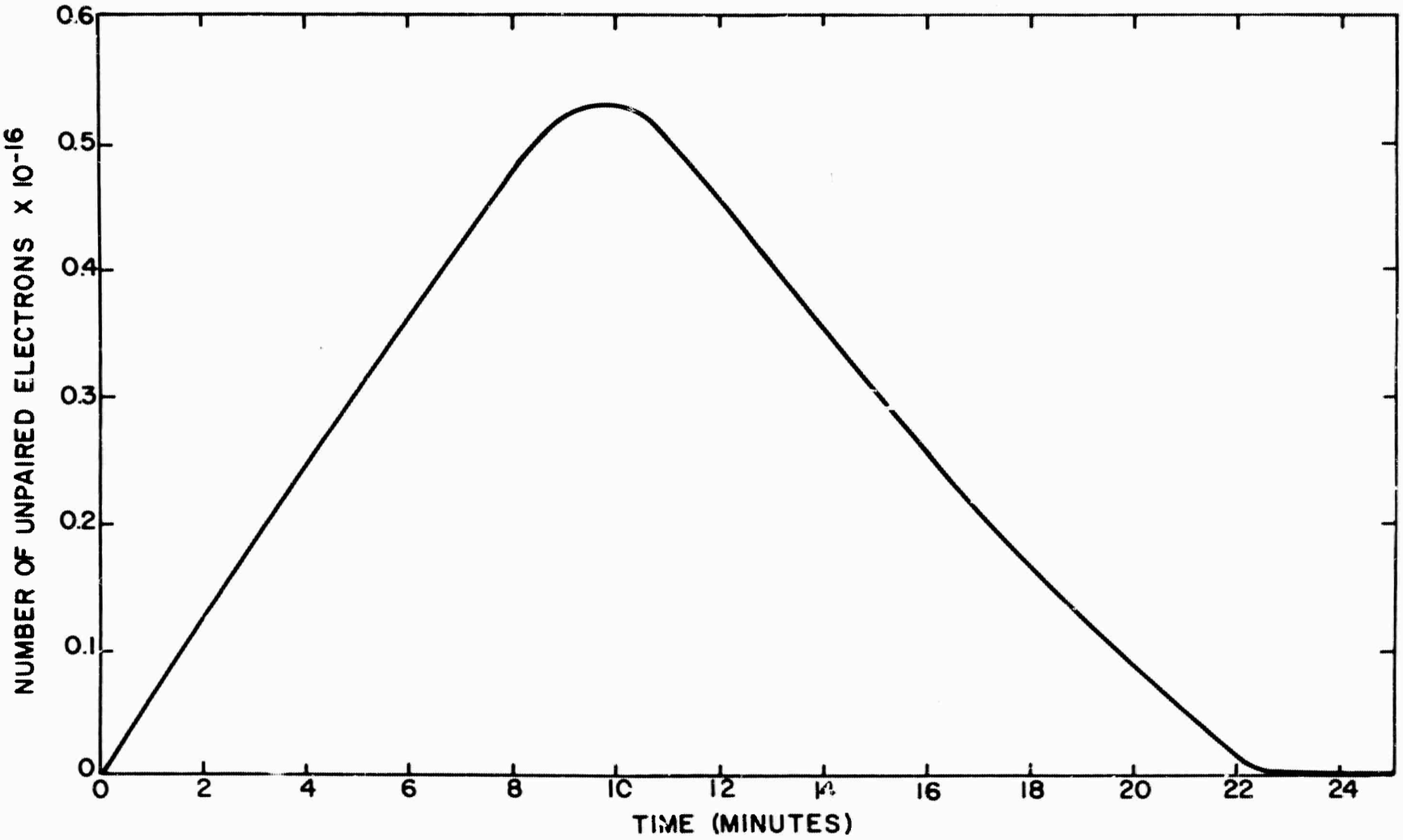

Fig. 8 - Continued Photolysis of Liquid OF_2 at 77°K

The effect of the presence of oxygen on the results of these experiment is difficult to assess at this time. However, since it is possible that oxygen may alter the mechanism of the photolytic reactions, or may broaden the EPR signal, rigorous measures described in Section A were undertaken to affect its removal.

The lack of an EPR signal in the spectra of samples chromatographed in the absence of light is strong evidence that liquid OF_2 is not paramagnetic. In addition, one would expect a hyperfine triplet from a paramagnetic species such as OF_2 rather than the observed doublet. Considering the system involved, a doublet could arise from $O_xF\cdot$ or $F\cdot$ radicals due to hyperfine interaction with the fluorine nucleus having a spin of 1/2. However, it is to be expected that the fluorine atom would react (to form F_2) much more rapidly than would the $CF\cdot$ radical. The fluorine radical has not been observed in the condensed phase, but has been observed in the gas phase[13] as six well-spaced resonances around a g-value of 4/3, with the lowest component appearing at 4159 gauss. A frequency of 9.249 Gc. was used.

We also have studied the EPR of liquid F_2 at 77°K. Tank fluorine and fluorine run through an HF trap and distilled have exhibited a weak signal with a linewidth of about 75 gauss and a g-value near 2.0. The signal strength increases with photolysis and seems to broaden. It is probable that the observed resonances in liquid fluorine are due to impurities. Present efforts to chromatograph liquid fluorine are being made more difficult by the high vapor pressure (280 mm. Hg) of F_2 at 77°K.

The small value of the coupling constant in OF_2 (13.5 gauss) is not what one would expect from hyperfine interaction of an electron with a fluorine radical. As a comparison, the hyperfine splitting due to two equivalent fluorine nuclei in liquid $NF_2\cdot$ is 64+2 gauss.[14] The hyperfine interaction due to a fluorine radical should be large, since the value calculated by assuming that the unpaired electron wholly in the 2s orbital of the fluorine atom is 17,050 gauss.[15] From a consideration of the above arguments, it is quite probable that the unpaired electron species is $O_xF\cdot$.

The most obvious radical species in photolyzed OF_2 is $OF\cdot$, from the dissociation $OF_2 \xrightarrow{h\nu} OF\cdot + F\cdot$. However, we cannot uniquely identify the number of oxygens on the radical at this time. $^{17}OF_2$ is being prepared to make possible a more unambiguous identification of the paramagnetic species in photolyzed liquid OF_2.

13/ N. Vanderkooi, Jr., and J. S. MacKenzie, Adv. Chem. Series, 36, 98 (1962).
14/ H. E. Doorenbos and B. R. Loy, J. Chem. Phys. 39, 2393 (1963).
15/ J. R. Morton, Chem. Revs., 64, 453 (1964).

The kinetics of the photolysis reaction suggests the following as possible reactions:

(1) $OF_2 \xrightarrow[\text{chain}]{h\nu} OF\cdot + F\cdot$

(2) $2\ F\cdot \longrightarrow F_2$

(3) $OF\cdot + M \xrightarrow{h\nu} R$

(4) $OF\cdot \xrightarrow{h\nu} R'$

(5) $OF\cdot + N \longrightarrow R''$

As the temperature is increased, the photolysis proceeds more rapidly. More energy is available to increase the rate of reaction (1). In addition, dependent upon the temperature, reaction (1) must be able to proceed in the absence of light. Hence, the continued increase in the rate of formation at 77°K after the lamp is extinguished. Reaction (3) and/or reaction (4) are the photolytic decay schemes which compete with reaction (1) when the lamp is on. With the lamp off at 77°K, the rate of formation increases rapidly for a short while, then drops back to a lower rate. This behavior can be explained by the fact that reactions (3) and (4) are not operating in the absence of light. Of course, other slower temperature dependent decay schemes may be operating, i.e., reaction (5).

At higher temperatures, (87°K, 100°K, 105°K) the decay of the signal is slow in the absence of light. Finally, at 120°K, the signal decays more rapidly after photolysis. The rate of the decay reactions must then be both temperature and photolytically dependent.

In Fig. 8 it is seen that continued photolysis causes the signal to reach very low levels. Thus, there must be a critical concentration which allows decay processes to predominate over the formation reactions.

The EPR studies on OF_2-NF_3 are now in progress. No resonance signal is observed in equimolar mixtures of OF_2 and NF_3. However, photolysis of the mixture results in an EPR signal. This signal, like that of pure OF_2 increases linearly (at a slower rate) with time during photolysis. (Photolysis of liquid NF_3 does not produce a resonance signal.) The temperature and concentration dependence of this photolytic system are being determined.

In addition, EPR studies have begun on O_2F_2 and O_3F_2. The results from this work are not considered reliable at this time because considerable decomposition of the materials took place during the actual resonance measurements, and the materials were not prepared in the complete absence of room light. Both of these faults have been remedied and results on these materials will be presented in the next report.

III. FUTURE WORK

During the next quarter the visible-UV spectra of liquid OF_2, NF_3 OF_2-NF_3, O_2F_2, O_3F_2 and N_2F_4 will be examined. The studies will include the effect of photolysis on the spectra, and a more accurate determination of the extinction coefficients. The infrared studies will continue; the systems above will be studied.

The EPR work will also continue with the investigation of O_3F_2, O_2F_2 and various systems (mixtures). The emphasis in these studies will be on the determination of mechanism of the observed photolytic behavior. A brief study of $^{17}OF_2$ will also be made.

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